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## PROCESS TO PREPARE SYNTHESIS GAS

Field of the invention

5 The invention is directed to a process to prepare a mixture comprising carbon monoxide and hydrogen from a carbonaceous feed by performing a partial oxidation reaction and an endothermic steam reforming reaction.

Background of the invention

10 EP-A-168892 describes an endothermic steam reforming reaction, which is carried out in a fixed bed situated in at least one pipe in which a temperature of between 800 and 950 °C is maintained by routing at least part of the hot product gas from a partial oxidation reaction along the pipe(s). According to this publication the combined partial oxidation and endothermic production of synthesis gas result in a better yield of synthesis gas, an  
15 increased H<sub>2</sub>/CO ratio, a lower usage of oxygen per m<sup>3</sup> of synthesis gas product obtained and a lower capital cost of the plant for the production of CO and H<sub>2</sub>-containing gas mixtures (as compared to partial oxidation).

20 A reactor and process for performing a steam reforming reaction is described in DE-A-3345088. This publication describes a reactor vessel for performing a steam reforming reaction starting from a natural gas feedstock. The vessel consisted of a tube sheet from which a plurality of tubes filled with a suitable  
25 catalyst extended into the vessel. The required heat of reaction is provided by passing the hot effluent of a partial oxidation reaction of natural gas at the exterior of the reactor tubes in the vessel. Such steam reformer

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reactors are also referred to as so-called convective steam reformer (CSR) reactors.

EP-A-983964 describes a convective steam reforming reactor vessel, wherein the vessel is provided with a plurality of reactor tubes containing a catalyst bed. Around the reactor tubes an annular sleeve is provided to transport a hot effluent of an auto thermal reformer (ATR). By indirect heat exchange between this hot effluent and the reactants passing through the catalyst bed the steam reforming reaction can take place.

A disadvantage of the processes of the prior art is that the obtained synthesis gas, carbon monoxide and hydrogen mixture, comprises of a relatively high content of steam. This steam is not desired, especially when the synthesis gas is to be used in a Fischer-Tropsch synthesis. Operating a CSR at a lower steam to carbon ratio is possible. However this will result in that less methane will be converted in the CSR reactor resulting in a synthesis gas containing a high level of methane. Although such levels may be acceptable for some processes, if the synthesis gas is to be used as feed to a Fischer-Tropsch process the presence of methane is not desirable because it will be present as an inert occupying reactor space.

The object of the present invention is to provide a process wherein the CSR reactor can be operated at a lower steam to carbon ratio and wherein the methane content in the resulting synthesis gas is kept at a lower level such that the synthesis gas can be used for example advantageously as feed for a Fischer-Tropsch reaction.

#### Summary of the invention

This object is achieved with the following process. Process for the preparation of hydrogen and carbon

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monoxide containing gas from a carbonaceous feedstock by performing the following steps:

- 5 (a) partial oxidation of a carbonaceous feedstock in a vertically oriented tubular partial oxidation reactor vessel comprising a burner at its upper end thereby obtaining a first gaseous mixture of hydrogen and carbon monoxide,
- 10 (b) catalytic steam reforming a carbonaceous feedstock in a Convective Steam Reformer comprising a tubular reactor provided with one or more tubes containing a reforming catalyst, wherein the steam to carbon molar ratio of the feed to step (b) is below 1, to obtain as separate product a steam reforming product,
- 15 (c) feeding the steam reformer product to the upper end of the partial oxidation reactor to obtain a mixture of the effluent of step (a) and the steam reformer product, and
- 20 (d) providing the required heat for the steam reforming reaction in step (b) by convective heat exchange between the mixture obtained in step (c) and the steam reformer reactor tubes thereby obtaining a hydrogen and carbon monoxide containing gas having a reduced temperature.

Applicants found that by feeding the steam reformer effluent obtained in step (b) to the upper part of the partial oxidation reactor vessel a large portion of the unconverted methane is converted to carbon monoxide and hydrogen due to the fact that methane will be partially oxidized by the burner also present in that part of the partial oxidation reactor vessel.

30 Description of the Figures

Figure 1 illustrates a CSR reactor vessel which may be used in the present invention.

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Figure 2 illustrates the combination of the reactor vessel of Figure 1 and a partial oxidation reactor vessel.

5 Figure 3 illustrates an integrated process involving the installation of Figure 2, a Fischer-Tropsch synthesis and some of its downstream unit operations.

Detailed description of the invention

10 The carbonaceous feedstock in step (a) is preferably a gaseous hydrocarbon, suitably methane, natural gas, associated gas or a mixture of C<sub>1-4</sub> hydrocarbons. Examples of gaseous hydrocarbons are natural gas, refinery gas, associated gas or (coal bed) methane and the like. The gaseous hydrocarbons suitably comprises mainly, i.e. more than 90 v/v%, especially more than 94%,  
15 C<sub>1-4</sub> hydrocarbons, especially comprises at least 60 v/v percent methane, preferably at least 75 percent, more preferably 90 percent. Preferably natural gas or associated gas is used. Preferably any sulphur in the feedstock is removed.

20 Preferably the carbonaceous feed in both steps (a) and (b) is a gaseous feed as described above. In such a preferred embodiment from 10 to 90 wt%, more preferably from 20 to 50 wt%, of the total gaseous feed to steps (a) and (b) is fed to step (b).

25 In step (a) the partial oxidation may be performed according to well known principles as for example described for the Shell Gasification Process in the Oil and Gas Journal, September 6, 1971, pp 85-90. Publications describing examples of partial oxidation  
30 processes are EP-A-291111, WO-A-9722547, WO-A-9639354 and WO-A-9603345. In such processes the feed is contacted with an oxygen containing gas under partial oxidation conditions preferably in the absence of a catalyst.

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The oxygen containing gas may be air (containing about 21 percent of oxygen) and preferably oxygen enriched air, suitably containing up to 100 percent of oxygen, preferably containing at least 60 volume percent oxygen, more preferably at least 80 volume percent, more preferably at least 98 volume percent of oxygen. Oxygen enriched air may be produced via cryogenic techniques, but is preferably produced by a membrane based process, e.g. the process as described in WO 93/06041.

Contacting the feed with the oxygen containing gas in step (a) is preferably performed in a burner placed in a reactor vessel. To adjust the  $H_2/CO$  ratio in the gaseous product obtained in the partial oxidation reaction in step (a), carbon dioxide and/or steam may be introduced into the feed. Preferably up to 15% volume based on the amount of gaseous product, preferably up to 8% volume, more preferably up to 4% volume, of either carbon dioxide or steam is added to the feed. As a suitable steam source, water produced in an optional downstream hydrocarbon synthesis may be used.

The gaseous product of the partial oxidation reaction in step (a) typically has a temperature of between 1100 and 1500 °C and an  $H_2/CO$  molar ratio of from 1.5 up to 2.6, preferably from 1.6 up to 2.2. By feeding the steam reformer product close to the burner the resulting temperature in said upper region will be suitably from 800 up to 1050 °C.

Step (b) may be performed by well-known steam reforming processes, wherein steam and the gaseous hydrocarbon feed are contacted with a suitable reforming catalyst in a CSR reactor. The convective steam reactor preferably comprises of a tubular reactor vessel provided with one or more tubes containing a reforming catalyst.

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Various designs for such a reactor are known and suited for the present invention. The design should be such that the steam reformer product and the synthesis gas used to provide heat are obtained as separate streams in such a reactor. Examples of such a reactor concept is described in US-A-6224789. Alternatively a design such as illustrated in Figure 1 may be applied.

Figure 1 illustrates a CSR reactor. The reactor space is defined by one or more parallel positioned reactor tubes (21) filled with a bed (22) of steam reforming catalyst, comprising a passageway (23) for hot gas. A third tube sheet (32) is present at the lower end of the reactor vessel (44) defining a space (33) which fluidly connects the vessel inlet (38) for the mixture as obtained in step (c) with the inlet of the passageways (23) which penetrate the tube sheet (32) via openings (34) which are preferably larger than the passageway (23) itself. The fact that the passageways are not fixed in the tube sheet (32) is advantageous because it allows the combined reactor tubes (21) and passageways (23) to freely thermally expand in the reactor vessel (44) at start-up and cool down situations. The lower ends of the passageway which extends into the lower space (33) may preferably be made from heat resistant materials like for example ceramics because of the high temperatures present in said space due to the fact that here the hot gaseous medium enters the reactor via vessel inlet (38).

The outlet opening (35) of the reactor tubes (21) comprising the catalyst bed (22) are positioned just above said tube sheet (32). The steam reforming product being discharged from said opening (35) will enter space (36) defined as the space between tube sheets (40)

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and (32). This space (36) fluidly connects the vessel outlet (39) for the steam reforming product with the openings (35). The space (36) may suitably be provided with flow directing baffles which will direct the flow of steam reforming product in a zig zag flow through said space thereby optimising the contact of the hot steam reformer product gas and the external surface of the reactor tubes (21) present in said space. In use part of the steam reforming product being discharged from openings (35) will leave the reactor vessel via outlet (39) and part will leave space (36) via openings (34) to space (33) by operating the reactor such that the pressure in space (36) is higher than the pressure in space (33). In use preferably from 0 to 60 wt% and more preferably from 0 to 40 wt% of the steam reformer product, as being discharged from openings (35), may enter space (33) to be mixed with the hot gaseous medium. This is advantageous because the steam to carbon ratio of the gases flowing in the passageways (23) can be increased thereby limiting metal dusting within the passageways (23).

Figure 1 further shows a vessel inlet (43) for natural gas and steam, a vessel inlet for a hot gaseous medium (38), a vessel outlet (39) for steam reforming product and a vessel outlet (42) for the gasses, which are emitted from the passageways (23). Tube sheets (40) and (41) are present in order to fix the reactor tubes (21) and to define collecting space (45) for the gasses emitted by the passageways (23) and an inlet space (46) fluidly connecting the vessel inlet (43) for steam and natural gas and the reactor tubes (21) comprising the catalyst bed (22).

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The catalyst and process conditions as applied in the steam reformer reactor tubes may be those known by the skilled person in the field of steam reforming. Suitable catalysts comprise nickel optionally applied on a carrier, for example alumina. The space velocity of the gaseous feed is preferably from 700 to 1000 litre (S.T.P.)/litre catalyst/hour, wherein S.T.P. means Standard Temperature of 15 °C and pressure of 1 bar abs. The steam to carbon (as hydrocarbon and CO) molar ratio is below 1 and preferably from 0.5 up to 0.9. If such low steam to carbon ratios are applied in step (b) the catalyst preferably comprises a Group VIII metal. More preferably the catalyst comprises (a) an oxidic support material and (b) a coating comprising between about 0.1 and about 7.0 wt% of at least one of the metals of the group consisting of Pt, Ni, Pd and Co, preferably platinum; said support material comprising:

(i) at least 80 wt% of  $ZrO_2$  which has been calcined at a temperature up to about 670 °C before the application of said coating; (ii) 0.5-10 mol% of at least one oxide selected from the group consisting of Y, La, Al, Ca, Ce and Si, preferably  $La_2O_3$ . Examples of such catalysts are for example the catalyst described in EP-A-695279. Preferably the feed also comprises an amount of  $CO_2$ , wherein preferably the  $CO_2$  over carbon (as hydrocarbon and CO) molar ratio is from 0.5 up to 2. The product gas of step (b) preferably has a temperature of from 600 up to 1000 °C and an  $H_2/CO$  molar ratio of from 0.5 up to 2.5.

The temperature of the hydrogen and carbon monoxide containing gas is preferably reduced in step (b) from a temperature of from 1000 up to 1500 °C after performing step (a) to a temperature of between 800 up to 1050 °C



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after performing step (c) to a temperature from 300 up to 750 °C after performing step (d). The temperature of the metal wall surfaces of the materials of the internals in the CSR reactor are preferably maintained below 1100 °C.

5        Optionally the mixture of the effluent of step (a) and the steam reformer product as obtained in step (c) may be subjected to a autothermal reformer step, also referred to as post catalytic reformer step, at the elevated temperatures of said mixture to convert the  
10        gaseous mixture obtained in step (c) to a mixture having a H<sub>2</sub>/CO molar ratio closer to the desired thermal equilibrium H<sub>2</sub>/CO molar ratio values valid for said operating temperatures. The combined mixture, optionally after performing such a post reforming step, is used in  
15        step (d).

      The above embodiment is illustrated in Figure 2. Figure 2 shows a CSR reactor vessel. For clarity reasons no internals of vessel (44) are shown in Figure 2. Also shown is a partial oxidation reactor (51) provided with a  
20        burner (52). A carbonaceous feed (50) and an oxygen containing gas (50') is supplied to burner (52). Also shown is that the product gas (55) of step (b) is fed to the upper half of the reactor vessel (51).

      Preferably the steam reformer product (55) is fed  
25        close, i.e. in the upper half of vessel (51), to the burner (52) in order to benefit the most of the resultant elevated temperatures of from 800 up to 1050 °C present in that region of the vessel (51). The methane content in steam reformer product (55) may be  
30        between 5 and 30 mol% carbon relative to the carbon as hydrocarbon in the feed to step (b), (43). This relatively high methane content is a resultant when operating step (b) at low steam to carbon ratio as

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described before. Because a methane slip will be corrected by the process of the current invention a lower reaction temperature in the CSR reactor tubes may also be allowed. A lower reaction temperature will also result in than more non-reacted methane will be part of product (55). Low temperatures in step (b) are suitably between 700 and 800 °C as measured on steam reformer product (55) as it leaves the reactor (44). A low temperature is desirable for material strength reasons for the internals used in reactor (44).

Figure 2 also shows a preferred autothermal reformer or post catalytic reformer catalyst bed (53) as present in the lower half of reactor vessel (51). The catalyst bed (53) may be any well-known reformer catalyst, for example a Ni-containing catalyst. The effluent of optional catalyst bed (53) is subsequently fed to inlet (38) of vessel (44), wherein the gasses are cooled in the passageways (23) (not shown in this Figure) and obtained as the final synthesis gas product (63) via outlet (42).

The synthesis gas (63) as obtained by the above process may advantageously be used as feedstock for a Fischer-Tropsch synthesis process, methanol synthesis process, a di-methyl ether synthesis process, an acetic acid synthesis process, ammonia synthesis process or to other processes which use a synthesis gas mixture as feed such as for example processes involving carbonylation and hydroformylation reactions. To steps (a) and (b) preferably recycle gases are fed. These recycle gasses are obtained in, for example the above exemplified, processes which use the synthesis gas as prepared by the process according to the invention. These recycle gasses may comprise C<sub>1-5</sub> hydrocarbons, preferably C<sub>1-4</sub>

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hydrocarbons, more preferably C<sub>1-3</sub> hydrocarbons. These hydrocarbons, or mixtures thereof, are gaseous at temperatures of 5-30 °C (1 bar), especially at 20 °C (1 bar). Further, oxygenated compounds, e.g. methanol, dimethylether, acetic acid may be present.

The invention is especially directed to the above process for the preparation of hydrogen and carbon monoxide containing gas (synthesis gas), wherein additional steps (e) (f) and (g) are also performed. In step (e) the synthesis gas is catalytically converted using a Fischer-Tropsch catalyst into a hydrocarbons comprising stream. In step (f) the hydrocarbons comprising stream of step (e) is separated into a hydrocarbon product and a gaseous recycle stream. Suitably the hydrocarbon product are those having 5 or more carbon atoms, preferably having 4 or more carbon atoms and more preferably having 3 or more carbon atoms. The gaseous recycle stream may comprise normally gaseous hydrocarbons produced in the synthesis process, nitrogen, unconverted methane and other feedstock hydrocarbons, unconverted carbon monoxide, carbon dioxide, hydrogen and water.

In step (f) the recycle stream is fed to step (a) and/or (b). Preferably the recycle stream is supplied to the burner of step (a) or directly supplied to the interior of the partial oxidation reactor.

Optionally part or all of the carbon dioxide present in such a recycle stream is separated from said recycle stream before being fed to step (a). Part of the carbon dioxide may suitably be fed to step (a).

Step (e) and (f) may be performed by the well known Fischer-Tropsch processes which are for example the Sasol process and the Shell Middle Distillate Process. Examples

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of suitable catalysts are based on iron and cobalt. Typical reactor configurations include slurry reactors and tubular reactors. These and other processes are for example described in more detail in EP-A-776959,  
5 EP-A-668342, US-A-4943672, US-A-5059299, WO-A-9934917 and WO-A-9920720.

Figure 3 illustrates the configuration of Figure 2 in combination with a Fischer-Tropsch synthesis process unit (64) and its downstream hydroconversion  
10 unit(s) (66), i.e. step (g). In addition to Figure 2 Figure 3 shows how the synthesis gas (63) is fed to Fischer-Tropsch synthesis process unit (64). In unit (64) a gaseous recycle stream (54) is separated from the hydrocarbon product (65) and recycled to partial  
15 oxidation reactor (51). Also shown is how part (60) of the steam reformer product (55) having a relatively high hydrogen over CO molar ratio is fed to a hydrogen recovery unit to obtain hydrogen (62) suitably for use in hydroprocessing unit(s) (66). In said units the  
20 hydrocarbon product present in (65), comprising typically a relatively large portion of compounds boiling above 370 °C, is converted by well-known hydrocracking and hydroisomerisation processes to middle distillates. Any remaining residue may be further converted to base oils  
25 by catalytic dewaxing processes (not shown), which also require hydrogen. Examples of such downstream hydroprocessing units are described in for example WO-A-0107538, WO-02070631, WO-02070629 and WO-02070627 and in the references cited in these publications.

30 The following examples will illustrate how the reactor according to the invention may be used in a process to make a mixture of carbon monoxide and hydrogen. The values presented are calculated values which will come close to

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the actual values because use has been made of well known thermodynamic relations known to the skilled person in the field of gasification and steam reforming.

Comparative Example 1

5       To a steam reformer reactor according to Figure 3 natural gas and steam are fed in a steam to carbon ratio of 0.75. Also a hot effluent of a partial oxidation reactor is fed via 27 to said reactor. The mass flows, temperatures and resultant product streams are described  
10       in Table 1.

Comparative Example 2

Example 1 is repeated except that the steam to carbon ratio of the feed to the CSR reactor of Figure 3 was equal to 1.

15       Example 3

In this example the effluent of the reactor tubes was first fed to the partial oxidation reactor as is illustrated in Figure 2 (line 55). No catalyst bed 53 was present in the reactor 51.

Example 1: Parallel operation - steam to carbon ratio of 0.75									
Stream name	Feed to the partial oxidation reactor		Feed to the CSR reactor		Effluent of the partial oxidation entering the CSR reactor		Steam reformer product of the CSR reactor		
	flow rate	mol%	flow rate	mol%	flow rate	mol%	flow rate	mol%	mol%
Component	kmol/h	(dry)	kmol/h	(dry)	kmol/h	(dry)	kmol/h	(dry)	(dry)
Hexane	0	0.00	0	0.00	0	0.00	0	0.00	0.00
Pentane	0	0.00	0	0.00	0	0.00	0	0.00	0.00
Butane	44	0.11	13	0.12	0	0.00	0	0.00	0.00
Propane	186	0.46	56	0.52	0	0.00	0	0.00	0.00
Ethane	1,423	3.52	427	3.94	0	0.00	0	0.00	0.00
Methane	21,727	53.75	6,526	60.20	822	1.19	514	1.61	1.61
Hydrogen	613	1.52	184	1.70	42,624	61.63	20,786	64.91	64.91
Carbon Monoxide	0	0.00	0	0.00	23,604	34.13	7,171	22.39	22.39

Example 1: Parallel operation - steam to carbon ratio of 0.75											
Carbon											
Dioxide	267	0.66	3,368	31.06	1,149	1.66	3,285	10.26			
Nitrogen	886	2.19	266	2.45	886	1.28	266	0.83			
Argon	76	0.19	0	0.00	76	0.11	0	0.00			
Oxygen	15,201	37.60	0	0.00	0	0.00	0	0.00			
Steam	0	0.00	24,543	0.00	5,034	0.00	17,538	0.00			
Total	40,424	100.00	35,384	100.00	74,195	100.00	49,559	100.00			
Molecular											
Mass	22.99		20.32		12.53		14.51				
Temperature											
(°C)	353		420		1,273		1,027				
Pressure											
(bar)	71		73		70		70				

Example 2: Parallel operation - steam to carbon ratio 1.0

Stream name	Feed to the partial oxidation reactor		Feed to the CSR reactor		Effluent of the partial oxidation reactor entering the CSR reactor		Steam reformer product leaving the CSR reactor	
	flow rate	mol%	flow rate	mol%	flow rate	mol%	flow rate	mol%
Component	kmol/h	(dry)	kmol/h	(dry)	kmol/h	(dry)	kmol/h	(dry)
Hexane	0	0.00	0	0.00	0	0.00	0	0.00
Pentane	0	0.00	0	0.00	0	0.00	0	0.00
Butane	45	0.11	12	0.11	0	0.00	0	0.00
Propane	191	0.46	51	0.45	0	0.00	0	0.00
Ethane	1,456	3.52	387	3.40	0	0.00	0	0.00
Methane	22,227	53.73	5,908	51.93	822	1.16	200	0.63
Hydrogen	627	1.52	167	1.47	43,641	61.65	19,765	62.74



Example 2: Parallel operation - steam to carbon ratio 1.0											
Carbon Monoxide	0	0.00	0	0.00	0	0.00	24,167	34.14	6,608	20.98	
Carbon Dioxide	274	0.66	4,613	40.54	1,176	1.66	4,687	14.88			
Nitrogen	906	2.19	241	2.12	906	1.28	241	0.76			
Argon	78	0.19	0	0.00	78	0.11	0	0.00			
Oxygen	15,561	37.62	0	0.00	0	0.00	0	0.00			
Steam	0	0.00	32,573	0.00	5,151	0.00	25,816	0.00			
Total	41,365	100.00	43,951	100.00	75,941	100.00	57,316	100.00			
Molecular Mass	22.99		20.62		12.52		15.81				
Temperature (°C)	353		420		1,273		1,027				
Pressure (barg)	71		73		70		70				

Example 3: Serial operation - steam to carbon ratio 0.75									
Stream name	Feed to the partial oxidation reactor			Feed to the CSR reactor			Effluent of the partial oxidation reactor entering the reactor 44 of Figure 2 via product (55) in Figure 2		
	flow rate		mol%	flow rate		mol%	flow rate		mol%
	kmol/h			kmol/h			kmol/h		
Hexane	0		(dry)	0		(dry)	0		(dry)
Pentane	0		0.00	0		0.00	0		0.00
Butane	38		0.10	17		0.13	0		0.00
Propane	161		0.44	73		0.55	0		0.00
Ethane	1,232		3.34	554		4.23	0		0.00
Methane	18,815		51.06	8,453		64.55	313		2.86
Hydrogen	531		1.44	239		1.82	63,382		65.02
Carbon Monoxide	0		0.00	0		0.00	30,775		23.47

Example 3: Serial operation - steam to carbon ratio 0.75

Carbon Dioxide	232	0.63	3,415	26.08	4,323	4.32	3,018	7.76
Nitrogen	767	2.08	345	2.63	1,112	1.11	345	0.89
Argon	75	0.20	0	0.00	75	0.08	0	0.00
Oxygen	14,998	40.70	0	0.00	0	0.00	0	0.00
Steam	0	0.00	23,727	0.00	21,597	0.00	15,393	0.00
Total	36,851	100.00	36,822	100.00	121,577	100.00	54,287	100.00
Molecular Mass	23.44		20.21		13.23		13.71	
Temperature (°C)	389		420		1,273		1,027	
Pressure (barg)	71		73		70		70	
C-atoms	22,149		13,262		35,411		13,262	
H-atoms	85,391		85,819		171,210		85,819	
O-atoms	30,460		30,558		61,018		30,558	